# STUDY OF THE BEHAVIOUR OF INNOVATIVE MATERIALS IN LIQUID METAL ENVIRONMENT

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## Abstract

Austenitic steel 316L with applied coating was studied to find a suitable material for impeller of main circulation pump at working conditions of small modular lead fast reactor. The chemical compatibility of the materials to the liquid metal environment was evaluated in liquid lead environment containing oxygen to ensure the oxidation while simulating temperature cycling. The operating temperature was controlled to vary between 450 °C and 520 °C, which are the temperatures that can occur in the system. The tests were designed to verify the effect of the different thermal expansion of the steel and the coatings on the corrosion resistance of the system. Austenitic steel 316L was used as a reference material and coatings base on Ti, Al, and W applied by physical vapor deposition were used for corrosion resistance improvement. Microscopical investigation identified oxidation, solution-based attack (SBA), and Pb penetration into the material. The damage to the coatings depended on their chemical composition and structure of the coating. However, in general, the application of the coating increased the resistance of the surface to corrosion damage and the thermal cycling did not affect the adhesion of the coating to the steel.

**Keywords:** Corrosion, coating, austenitic steel, impeller, heavy liquid metal

## 1.    INTRODUCTION

Lead-cooled fast reactors (LFR) represent an innovative concepts of GEN IV reactors. Due to its high thermal conductivity, high boiling point, and large thermal capacity are heavy liquid metals (HLM) supposed to be an excellent cooling media for high temperature nuclear reactors. It was found that austenitic steels are not prone to liquid metal embrittlement as ferritic-martensitic steels. However, the issue of the corrosion resistance, which is crucial for the use of the steel as a structural material, also need to be solved [1-6]. Oxygen has been recognized as an effective non-metallic inhibitor of the corrosion in HLM and performance of austenitic steel at various temperatures and oxygen levels has been widely studied. It was found that Ni-containing alloys suffer from high mass transfer at elevated temperatures. The dissolution of nickel can be prevented by formation of the protective oxide layer using controlled oxygen content in the coolant. However, controlling, managing, and maintaining of the optimum oxygen concentration presents some difficulties, so the use of a protective coating is proving to be an effective way of a protecting the steel [7-10]. Of course, it is necessary to ensure both excellent adhesion of the coating to the substrate, compactness and homogeneity of the coating, and the coating should be made of the materials that are resistant to HLM environment.

## 2.    EXPERIMENTAL

Austenitic steel 316L was used as a reference material and three different coatings were applied on the reference material to improve the resistance to HLM environment. The coatings were prepared by Physical Vapour Deposition (PVD) and the composition of the coatings was chosen to ensure the material´s ability to form a protective layer and minimize oxidation of the base material. Coating AB was based on aluminium and titanium, coating V was based on tungsten and coating MARWIN was nanoscale AlTiN gradient system, which

was formed by a layer with a continuous change in composition. Surface morphology of the coatings can be seen in (**Figure 1**).
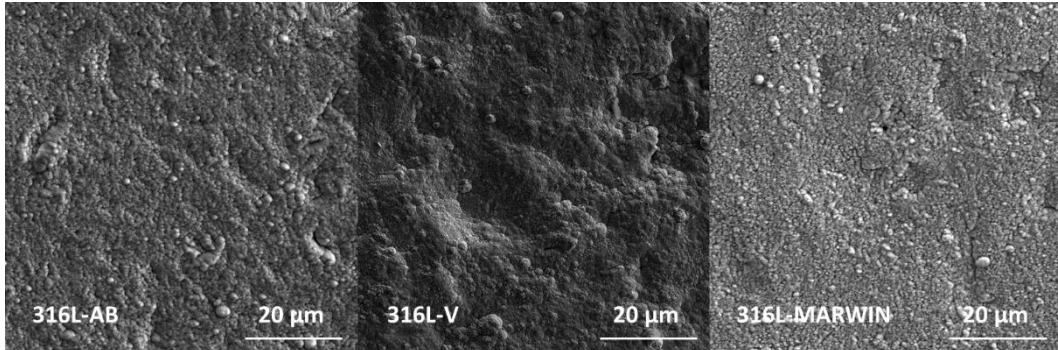


**Figure 1** Surface morphology of the coatings

Test was performed in an instrumented static tank, which consisted of a 4.5 l stainless-steel test chamber with inner alumina crucible. This crucible prevented the contamination of the environment by the corrosion products of the test chamber and the exposure of specimens was not affected. A reducing Ar+H$_2$ (6 %) gas mixture was used as a cover gas. Oxygen concentration was measured by using oxygen sensors based on Bi/Bi$_2$O$_3$ and Mo reference electrode. Active oxygen control, i.e., maintaining the oxygen concentration in Pb at the targeted level, was ensured by means of automatic mixing of cover gases (Ar+H$_2$ (6 %) with Ar+O$_2$ (10 %)) based on the oxygen sensor signal. Heating elements reeled onto the chamber outer surface allowed controlling the test temperature, while the thermal insulation of the whole setup minimized potential heat losses and high temperature gradient in the Pb bath, see (**Figure 2**). A ball valve separated the air-lock and the test chamber.

Test was performed in liquid lead environment containing 10$^{-6}$ wt.% of oxygen to ensure the oxidation conditions, the temperature varied between 450 °C and 520 °C. The lower and upper exposure temperature was maintained for 168 h and the temperature change lasted for 5 h. The test was terminated after 1000 h of the exposure. The temperature cycling was used to simulate changes which can occur due to sudden changes in the system.
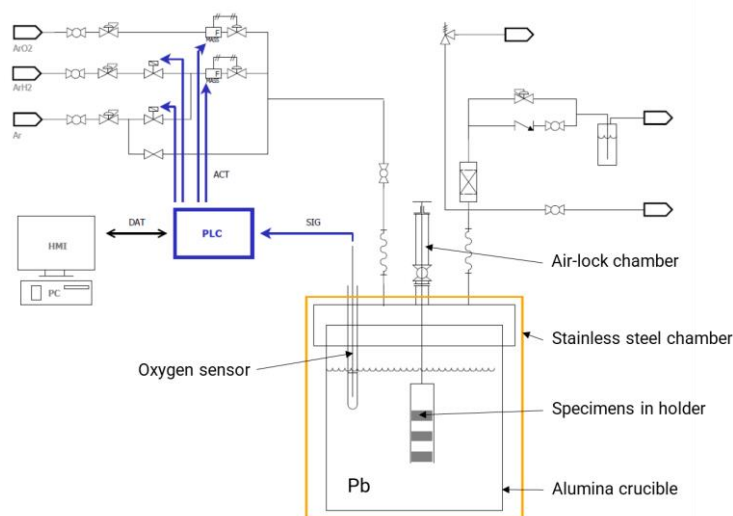


**Figure 2** Scheme of experimental setup

After the exposure in Pb, the corrosion coupons were investigated using Tescan LYRA3 XMU field emission scanning electron microscopes (SEM, Tescan, Brno, The Czech Republic), equipped with secondary electrons

(SE), the back-scattered electrons (BSE) and the energy-dispersive X-ray spectroscopy (EDS) detectors (Oxford Instruments, Abingdon, UK) controlled by means of the AZtec software.

## 3. RESULTS AND DISCUSSION

Post test SEM observation revealed that the corrosion mechanism of tested materials can be defined as a combination of inner oxidation and SBA with Pb penetration into the base material (**Figure 3**). Outer oxidation of 316L steel was found very sporadically in the form of nodules with the maximum thickness of 4.3 µm. Only 1 % of the surface was protected by outer oxide layer, which was not protective and did not prevent the formation of inner oxide, SBA, and Pb penetration into the base material. EDS mapping confirmed the depletion of the surface layer from Ni and slight increase of Cr concentration on the surface. Cr content was not sufficient to protect the steel from the SBA, results can be seen in (**Figure 4**).
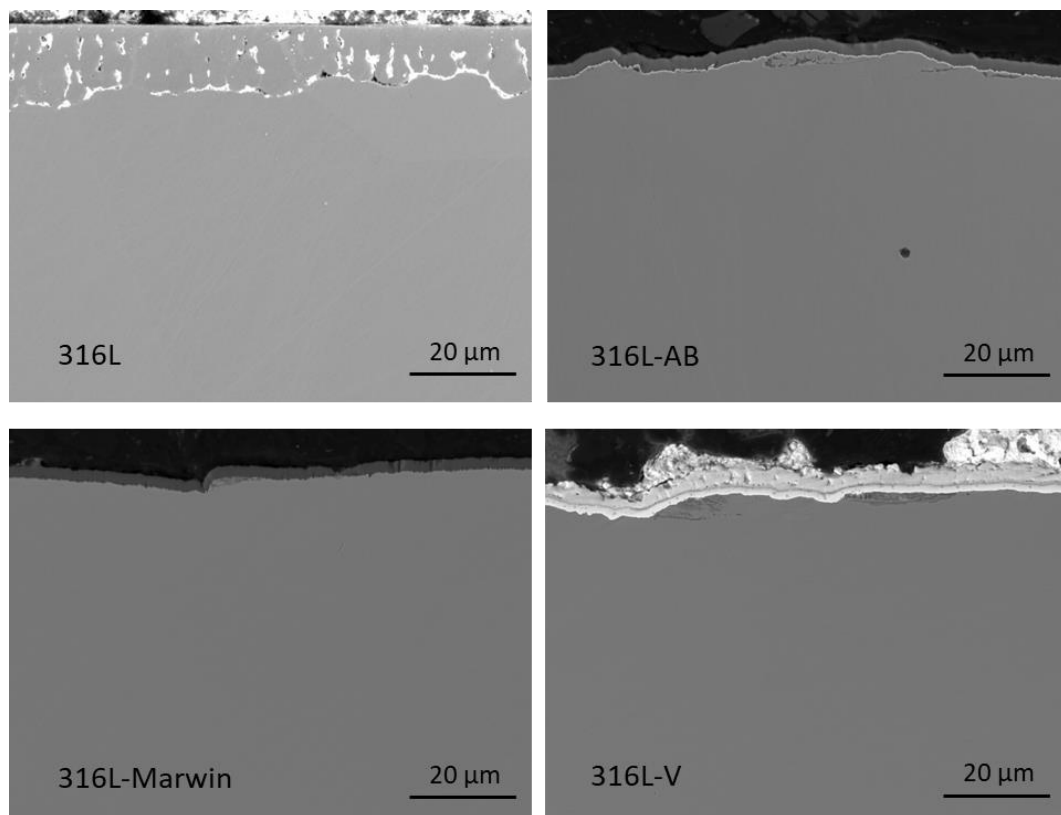


**Figure 3** Cross-section of 316L specimen and 316L covered by the coatings after the 1000 h of exposure, typical corrosion damage

Application of the coatings improved the resistance of 316L steel to the SBA and Pb penetration. As can be seen in (**Figure 2**), no SBA was found under the protective coatings. Applied coatings were dense and uniform. Coating AB and MARWIN were not affected by the exposure. Their structure was sufficiently dense to prevent the penetration of lead through the coating to the base material, but the columnar structure did not prevent the oxygen diffusion through the coating. SEM analysis revealed the inner oxidation due to the reaction of diffused oxygen with the base material on the coating/substrate interface (**Figure 3**). A different behaviour was observed for the 316L-V coating. The coating protected the substrate from the SBA and Pb penetration was not observed but severe oxidation was observed on the coating´s surface (**Figure 5**). Due to this oxidation, the thickness of the coating decreased, and the diffusion of oxygen and subsequent growth of inner oxide was more intense than for the coatings based on Al.
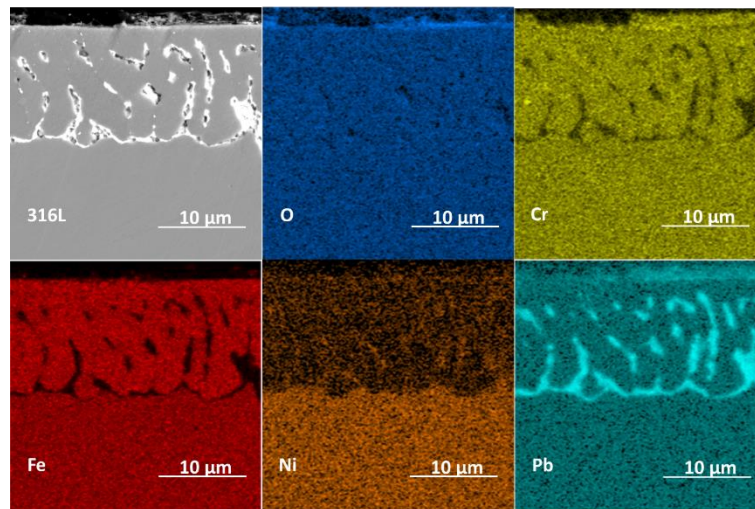
**Figure 4** Near-surface EDS elemental distribution in 316L steel 1000 h of exposure showing the Pb penetration and accompanying Ni depletion zone beneath it
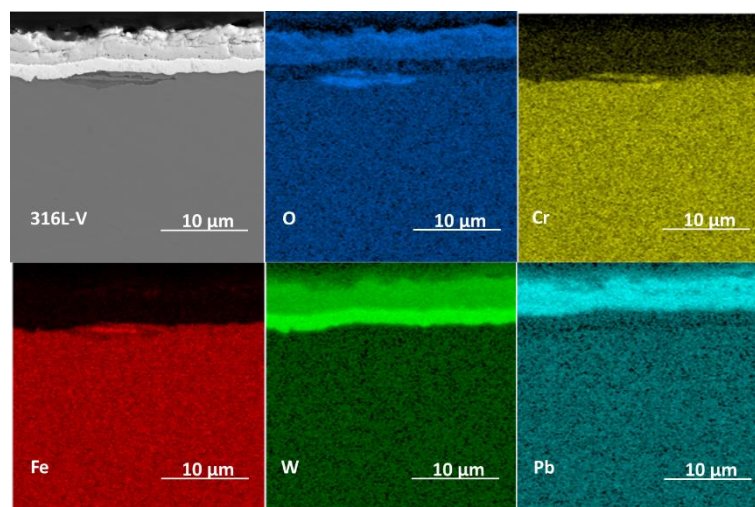


**Figure 5** EDS cross-section analysis of 316L_V specimen after 1000 h of exposure showing the degradation of the coating

For characterization of the corrosion degradation and determination of the corrosion depth, thirty evenly spaced images were captured along both sides, each having a 100 μm field-of-view. Ten measurements were acquired from each image. The relative frequency of the corrosion depth was calculated as a number of data falling into the corresponding interval of depths, divided by the total number of data points (300). The statistic evaluation revealed that almost 50 % of the 316L surface was affected by corrosion. The main degradation mechanism was SBA with average depth of 4.9 μm while inner oxidation depth reached up to 2.5 μm. Application of the coatings eliminated the SBA. Slight decrease of affected area was found in 316L-AB and 316L-V systems and five times lower depth of inner oxidation. A significant reduction in the area affected by the corrosion was found for 316L-MARWIN system. Average depth of inner oxidation was eight time lower than for reference. Results are summarized in **Table 1**.

**Table 1** Comparison of the corrosion resistance of 316L steel and protective coatings

| Specimen | Affected area (%) | Inner oxidation depth avg. / max. (µm) | SBA depth avg. / max. (µm) |
|---|---|---|---|
| 316L | 48 | 2.5 / 45.8 | 4.9 / 47.1 |
| 316L-AB | 31 | 0.6 / 6.1 | 0 |
| 316L-V | 31 | 0.5 / 4.7 | 0 |
| 316L-MARWIN | 12 | 0.3./ 8.4 | 0 |

Comparison of the corrosion resistance and all types of degradation with characteristic distribution can be seen in (**Figure 6**).
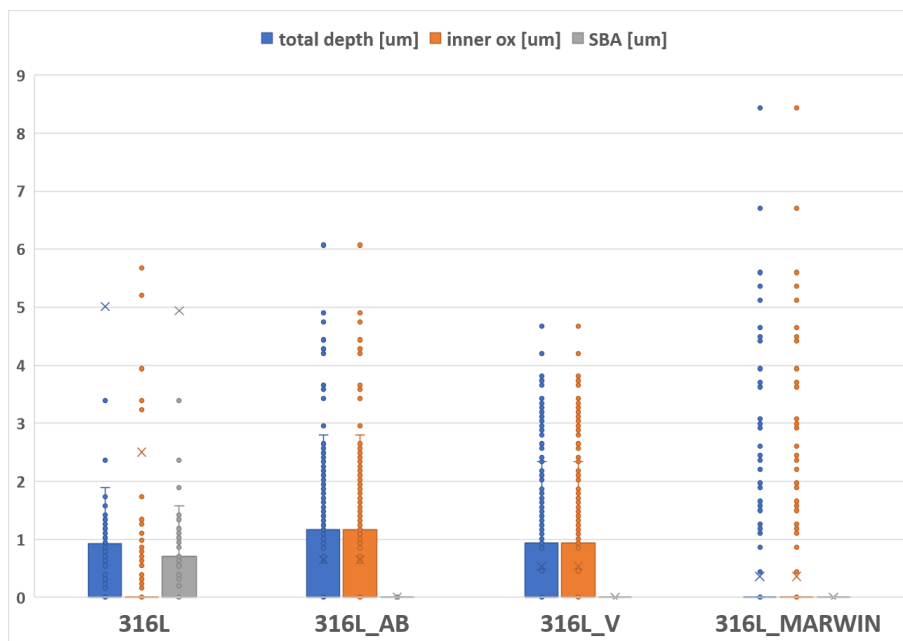


**Figure 6** Evaluation of corrosion, comparison of degradation mechanisms

## 4.    CONCLUSION

In this study the corrosion resistance of the protective coatings to HLM environment was evaluated. Austenitic steel protected by the PVD coatings was exposed to Pb environment with oxygen concentration $1x10^{-6}$ wt.% and the temperature varied from 450 °C up to 520 °C. It can be concluded that.

- Severe degradation of austenitic stainless steel without coating – SBA, Pb penetration, oxidation.

- No Pb penetration through the coatings.

- Decrease of the steel surface affected by the oxidation due to the coating.

- Significant influence of the coating composition on the protective ability.

- Coatings containing W are not suitable for HLM environment.

- MARWIN had four times less corroded surface with eight times lower depth of inner oxidation.

**REFERENCES**

[1]   ALEMBERTI, A., SMIRNOV, V., SMITH, C.F., TAKAHASHI, M. Overview of lead-cooled fast reactor activities, *Prog. Nucl. Energy*, 2014, vol. 77, pp. 300-307

[2]   CINOTTI, L., SMITH, C.F., SEKIMOTO, H., MANSANI, L., REALE, M., SIENICKI, J.J. Lead-cooled system design and challenges in the frame of Generation IV International Forum, *J. Nucl. Mater.*, 2011, vol. 415, pp. 245-253, doi: 10.1016/j.jnucmat.2011.04.042

[3]   FROGHERI, M., ALEMBERTI, A., MANSANI, L. The Advanced Lead Fast Reactor European Demonstrator (ALFRED). In: *International Topical Meeting on Nuclear Reactor Thermal-Hydraulics (NURETH-15)*. Pisa: 2013.

[4]   ALEMBERTI, A., CARAMELLO, M., FRIGNANI, M., GRASSO, G., MERLI, F., MORRESI, G., TARANTINO, M. ALFRED reactor coolant system design, *Nucl. Eng. and Design*, 2020, vol. 370, pp. 110884, doi: 10.1016/j.nucenqdes.2020.110884

[5]   CARAMELLO, M., FRIGNANI, M., GRASSO, G., TARANTINO, M., MARTELLI, D., LORUSSO, P., DI PIAZZA, I. Improvement of ALFRED thermal hydraulics through experiments and numerical studies, *Nucl. Eng. and Design*, 2023, vol. 4096, pp. 112365, doi: 10.1016/j.nucenqdes.2023.112365

[6]   DAMIANI, L., GIRIBONE, P., REVETRIA, R., PRATO, A.P. A passive decay heat removal system for the lead cooled fast reactor demonstrator "Alfred", *Prog. Nucl. Energy*, 2015, vol. 83, pp. 294-304

[7]   FAZIO, C., BENAMATI, G., MARTINI, C., PALOMBARINI, G. Compatibility tests on steels in molten lead and lead-bismuth, *J. Nucl. Mater.*, 2001, vol. 296, pp. 243-248

[8]   KOSEK, L., ROZUMOVA, L., HOJNA, A., APARCIO, C., VRONKA, M., VIT, J. Mechanism of localized corrosion issues of austenitic steels exposed to flowing lead with $10^{-7}$ wt.% oxygen at 480 °C up to 16,000 h, *J. Nucl. Mater.*, 2022, vol. 572, 154045

[9]   LI, X.N., LIANG, L.H., XIE, J.J., CHEN, L., WEI, Y.G. Thickness-dependent fracture characteristics of ceramic coatings bonded on the alloy substrates, *Surf. Coat. Technol.*, 2014, vol. 258, pp. 1039-1047

[10]  ZHANG, J. A review of steel corrosion by liquid lead and lead–bismuth, *Corros. Sci.*, 2009, vol. 51, pp. 1207–1227, doi: 10.1016/j.corsci.2009.03.013